

Claims

1. A time temperature indicator for indicating a temperature change over time, comprising at least one indicator compound in a first isomeric form, which is converted into second

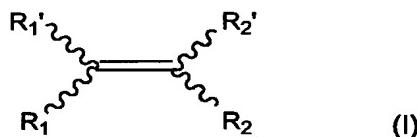
5 isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric or the second isomeric form of the indicator.

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2. The time-temperature indicator of claim 1, wherein the at least one indicator compound is a diarylethene or a spiroaromatic compound.

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3. The time-temperature indicator of of claim 2, wherein the diarylethene is a compound of Formula (I)



wherein

20 R1 and R2 each independently represent C6-C14 aryl, C4-C12 heteroaryl, conjugated heterocyclic; wherein said heteroaryl and conjugated heterocyclic may contain one to three heteroatoms selected from N, O, or S; and wherein said aryl, heteroaryl, or conjugated heterocyclic may be substituted by one or more halogen, hydroxyl, thiol, amino, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, -CH=CH-CN, azido, or amido;

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30 R1' and R2' each independently represent H, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, or amido; or substituted or unsubstituted C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-

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aromatic heterocyclic; or R1' and R2' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring or a C4-C7 heterocyclic ring containing one to three endocyclic or exocyclic heteroatoms selected from N, O, or S; said N heteroatom may be further substituted by H, or by one or two substituted or unsubstituted groups

5 selected from C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, or -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic or inorganic

10 anions, and optionally wherein said C5-C8 carbocycle is substituted by one or more halogen, preferably by one or more fluoro atoms; and optionally

R1, R1', R2 and R2' each independently represent a charged group or a group substituted by another group having a charge; said charge may be localized or delocalized and may be positive or negative;

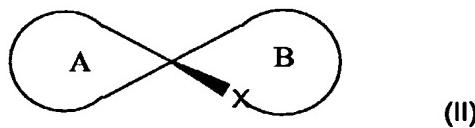
and wherein said R1 and R2 are in a cis or trans conformation.

4. The time-temperature indicator of claim 3, wherein the diarylethene is

20 (a) a symmetric diarylethene, preferably selected from the group consisting of 1,2-dicyano-1,2-bis(2,4,5-trimethylthiophene-3-yl)ethane (**1**); 2,3-bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride (**2**); 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene (**3**); and 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene (**4**); or

25 (b) an asymmetric diarylethene, preferably selected from the group consisting of 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl) maleic anhydride (**5**); and 2-(methoxybenzo[b]thiophene-3-yl)-3-(1,2-dimethyl-3-indolyl) maleic anhydride (**6**).

5. The time-temperature indicator of claim 2, wherein the spiroaromatic compound is a compound of Formula (II):



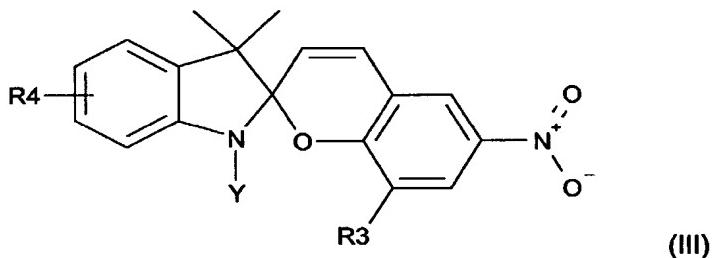
wherein

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- ring A represents a C5-C8 carbocycle, C4-C7 heterocycle containing at least one heteroatom selected from N, O, or S; said N heteroatom may be further substituted by one or two groups selected from C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 5 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, or -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic or inorganic anions;
- 10 said C5-C8 carbocycle or C4-C7 heterocycle may be substituted by one or more of the groups selected from halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, azido, amido or amino;
- 15 ring B represents a substituted or unsubstituted heterocycle containing at least one heteroatom X, said X being selected from N, O, and S; wherein said N atom may be further substituted by one or two groups selected from C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 20 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic; hydroxyl, or -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic or inorganic anions;
- 25 and wherein said ring B may contain one or more endocyclic double bonds and is optionally substituted by one or more halogen, preferably by one or more fluoro atoms;
- said rings A and B may be fused to one or more substituted or unsubstituted carbocycle, C4-C14 heterocycle, C6-C14 aryl or C4-C14 heteroaryl ring system;
- 30 and wherein the compounds of Formula II may be neutral, charged, multiply charged, positively charged having an external anion, negatively charged having an external cation or zwitterionic.

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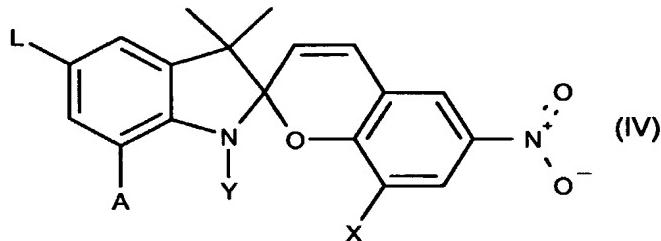
6. The time-temperature indicator of claim 5, wherein the spiroaromatic compound is a spiropyran derivative, preferably selected from the group consisting of 1',3',3',8-tetramethyl-5-hydroxymethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole) and 1',3',3',8-tetramethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole).
- 5 7. The time-temperature indicator of claim 5, wherein the spiropyran derivative is a derivative of 1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-2H-indole) of Formula (III):



- 10 wherein
- R3 is selected from the group consisting of H, halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, or azido; wherein said alkyl, alkenyl, alkynyl, aryl, heteroaryl, and non-aromatic carbocycle may be substituted by one or more group selected from halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, or sulfo;
- 15 R4 is selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl or -CH=CH-CN; and
- 20 Y is selected from the group consisting of C1-C25 alkyl, preferably methyl, n-propyl and n-octadecyl, and C7-C15 aralkyl, wherein said alkyl and aralkyl may be substituted by one or more group selected from halogen, preferably fluorine.
- 25 8. The time-temperature indicator of Claim 5, wherein the spiroaromatic compounds include at least one of the following: spirooxazine or its derivatives, spironaphthoxazine or its derivatives, and spiroindolinopyridobenzoxazine or its derivatives.

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9. A spiroaromatic compound of general Formula (IV):



wherein

A and L are independently of each other selected from the group consisting of H,

- 5 halogen, C₂-C₁₂ alkenyl, C₂-C₁₂ alkynyl and $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{R} \end{array}$, wherein R is C₁-C₆ alkyl, C₁-C₆ alkoxy, C₆-C₁₄ aryl and C₇-C₁₅ aralkyl; wherein said alkenyl, alkynyl and
may be substituted by one or more group selected from halogen, hydroxyl, thiol, amino,
alkoxy, nitro, azido, sulfo, aryl and heteroaryl;
- Y is selected from the group consisting of C₁-C₂₅ alkyl and C₇-C₁₅ aralkyl, wherein
10 said alkyl and aralkyl may be substituted by one or more group selected from halogen,
preferably fluorine; and
X is C₁-C₆ alkoxy or L;
with the proviso that Y is not n-propyl when L, A and X are hydrogen.

- 15 10. The spiroaromatic compound of claim 9, wherein
L is hydrogen, Cl, Br or I;

Y is methyl, n-propyl, n-octadecyl or ;
X is hydrogen or methoxy; and
A is hydrogen;

20 with the proviso that Y is not n-propyl when L and X are hydrogen.

11. A printing ink or printing ink concentrate, comprising the spiroaromatic compound of
claim 9 or 10.

- 25 12. A high molecular weight material, comprising the spiroaromatic compound of claim 9 or
10.

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13. A method of manufacturing a time-temperature indicator of any of claims 1 to 8 comprising the steps of
 - (a) embedding in or atop a matrix said at least one indicator compound; and
 - (b) inducing the formation of a metastable state of said embedded at least one indicator compound.
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14. The method of claim 9, further comprising the step of covering the time-temperature indicator with a cover support, preferably designed to avoid photo recharging and/or
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- photo bleaching.